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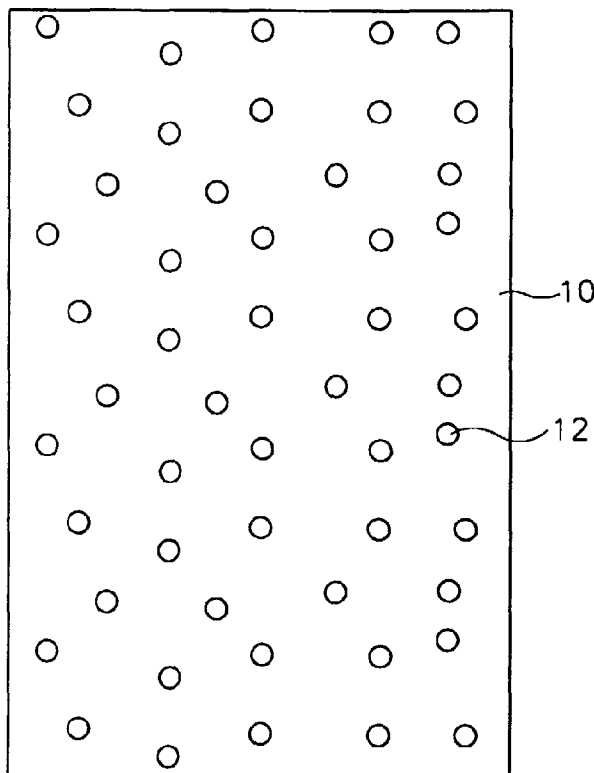
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(54) Title: POROUS SEPARATOR AND METHOD OF MANUFACTURING THE SAME



(57) Abstract: Disclosed are a porous separator on which a binder material is dispersed to facilitate an advantageous attachment with an electrode and a method of manufacturing the same. First, a solution containing a polymer binder is coated onto a porous polymer layer. Then, a solvent is removed to manufacture the separator. The polymer binder material bestows a good adhesive strength between the electrode and the separator. In addition, an electrolytic solution can be easily impregnated into the electrode and the separator through a space where the binder component is not present. An electro chemical cell manufactured by employing the separator has a high capacity and a stable cyclife characteristic.

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## POROUS SEPARATOR AND METHOD OF MANUFACTURING THE SAME

### Technical Field

5       The present invention relates to a porous separator applicable to an electrochemical cell and a method of manufacturing the same, and more particularly, to a porous separator on which a polymer binder component is dispersed at the surface portion thereof and a method of manufacturing the same.

### 10   Background Art

      An electric reduction of an active material of a cathode and an oxidation of an active material of an anode is induced during discharging of a charged cell or battery, and as the result electrons flow from the anode to the cathode through an external circuit for generating current. An electrolytic layer is present between the cathode  
15   and anode to prevent an internal flow of the electrons, which is called as an electric short, and to impart an ion transmission between the cathode and anode. The electrolytic layer should be made from a non-electron conductive material and transmit ions during discharging for a primary battery and during charging and discharging for a secondary battery. The electrolytic layer should be electro  
20   chemically and chemically stable with respect to the cathode and anode.

      Generally, an electrolytic layer is manufactured by filling a porous layer called as a separator with aqueous or non-aqueous electrolyte containing salts. As for the separator, porous polyethylene, polypropylene, rayon paper, pulp paper, glass fiber paper, and the like can be used. The separator is positioned as a porous free  
25   standing film between the cathode and anode. The separator is commonly manufactured by stretching a plastic film through repeating heating and cooling, or by extracting a soluble plasticizer or a filter from the plastic film, or through a

plasma oxidation of the plastic film.

Recently, a gel or a polymer electrolyte composed of a solvent, a salt and a polymer is used as for the electrolytic layer. U.S. Pat. Nos. 5,691,005 and 5,597,659 disclose a method of using a separator matrix by impregnating pores of a separator  
5 with a gel electrolyte having an ionic conductivity.

The separator should be porous, chemically stable, and flexible, thin and economic and have a good mechanical strength. These characteristics are essential in improving the cell capacity and rate capability in a winding-type or stacking-type cell.

10 Meantime, an electrode and an electrolyte should make a uniform contact in order to obtain a good cell performance. When the contact is not uniform, the electrochemical reaction at the electrode becomes non-uniform and the capacity and cyclife is reduced. Generally, when the polyolefin porous separator is used, the contact between the electrode and the separator is kept through a physical pressure.  
15 For the cell having the winding-type structure, the contact between the electrode and the separator is kept through a winding tension and for the Prismatic winding cell, an additional pressure by an external can is applied. However, when the contact between the electrode and the separator is kept only through a physical pressure, the shape of the cell is limited and therefore, a cell having various structures and areas  
20 cannot be manufactured.

On the contrary, when a gel or a polymer electrolyte is used as for the electrolytic layer, the interface between the electrode and the electrolytic layer can be kept uniformly without any physical pressure because the gel or polymer electrolyte has an adhesive strength to the electrode. Various methods for  
25 manufacturing the gel has been suggested. A laminating method of the polymer electrolyte through heating, a gelling method after impregnating a battery including a porous separator with an electrolytic solution which can form the gel, etc. can be

illustrated. When the gel or polymer electrolyte is used as for the electrolytic layer, a light and thin battery can be manufactured because the interface between the electrode and the electrolytic layer is kept stable and an energy density per weight and/or volume can be improved when comparing with a battery manufactured by using a metal can such as an aluminum pouch as for an external wrapper.

However, in order to achieve a uniform contact between the gel and polymer electrolyte with the electrode and to obtain a good ionic conductivity and a good mechanical strength of the electrolytic layer, various additional procedures are required when compared with the method employing only a separator as for the electrolytic layer. For example, in U.S. Pat. Nos. 5,460,904, 5,456,000 and 5,418,091, a cell is manufactured through a heat lamination of a polymer layer prepared from PVdF, silica particles and dibutyl phthalate (DBP) as a plasticizer, onto an electrode. Then, pores for impregnating an electrolytic solution is formed through dipping the cell into a solvent which can dissolve and extract DBP. Through the above-described method, the extracting process is required in order to increase the impregnating amount of the electrolytic solvent and a complete removal of the solvent used for the extraction of the plasticizer is difficult and needs a complicated process.

In U.S. Pat. Nos. 5,853,916, 5,716,421, 5,834,135, 5,681,357 and 5,688,293 (Motorola, Mitsubishi), a method of manufacturing a polymer battery by which the extracting process of the plasticizer is not needed, is disclosed. According to the disclosure, a polymer material is uniformly coated on a porous separator having a good mechanical strength and then is compressed onto the electrode with heat. Then, the cell is dipped into an electrolytic solution to swelling the polymer layer. According to this method, a good adhesive strength between the electrolyte and the electrode is kept and the process is simplified because the electrolytic solution is impregnated into the cell without an extracting process. However, a long period of

time is required for the absorption of the electrolytic solution into the compact polymer layer to reduce the productivity.

Japanese Patent Laid-Open Publication No. Hei 1-089054 (Mitsubishi Electric Corp.) discloses a method of adhering a cathode and anode onto a porous separator after coating a binder resin solution onto the porous separator. According  
5 to this method, the electrodes are adhered to the separator coated with the binder resin solution before an evaporation of a solvent and the solvent is evaporated at a temperature range of about 80°C or less. After evaporating the solvent, pores are formed at the resin layer and a binding layer having a porous structure is  
10 manufactured.

However, when the electrodes are adhered to the separator while the solvent remains, the preparation of the electrolyte and the adhering process of the electrode should be continuously implemented. In addition, since the adhering strength and the minute structure of the binding layer changes according to the evaporating  
15 degree of the solvent, a continuous manufacture of cells having a uniform structure is difficult.

U.S. Pat. Nos. 5,691,005 (Mitsubishi Electric Corp.) and 5,597,659 (Mitsubishi Electric Corp.) disclose a lithium secondary battery including an electrolytic layer having a separator filled with a gel-impregnated polymer  
20 components into a separator are cross-linked by exposing UV. However, some disadvantages are as follows. The electrolytic solution is evaporated and the physical properties of the separator manufactured by this method changes during storing. In addition, the cell should be manufactured within a drying room.

Japanese Patent Laid-Open Publication No. Hei 10-162802 (Sony Corp.)  
25 discloses a cell manufactured by impregnating a non-woven fabric or an insulating porous film with a liquid polymer material base on polyacrylonitrile to manufacture a separator and then positioning thus obtained separator between a cathode and

anode.

U.S. Pat. Nos. 5,853,916 (Motorola), 5,716,421 (Motorola), 5,834,135 (Motorola), 5,681,357 (Motorola) and 5,688,293 (Motorola) disclose a separator composed of a non-gelling porous layer and a gelling polymer layer and a secondary  
5 battery manufactured by using the same. In this case, a mechanical strength is accomplished and a short induced from a contact of the cathode and anode is prevented by the non-gelling porous separator layer as a non-active material which has a low affinity to an electrolytic solution. Meantime, the gelling layer positioned at one or both surface of the porous separator has a good affinity to the electrolytic  
10 solution and imparts an adhesive power to the electrode. In these patents, the gelling layer is formed through coating onto the separator, and so, the electrolytic solution is impregnated into the cell through diffusion into the gelling layer.

In U.S. Pat. No. 5,827,015 (Motorola), a polymer binder component such as PVdF is sprayed onto an electrode and then, a porous separator is compressed with  
15 heat to adhere the electrode and separator. The binder component present at the contacting surface of the electrode and the separator facilitates a good adhering strength between them. However, the spraying of the binder component onto the electrode might induce a non-uniform surface of an electrode. In addition, the sprayed material might be present at the inner portion of the electrode as well as at  
20 the surface portion of the porous electrode.

### **Disclosure of the Invention**

It is an object of the present invention to provide a porous separator having a good mechanical strength and a good adhering strength with an electrode.

25 Another object of the present invention is to provide a method of manufacturing the above-described porous separator.

Further another object of the present invention is to provide a method of

manufacturing a cell by which an adhering between a separator and an electrode is advantageous through employing the above-described porous separator.

Still further another object of the present invention is to provide an electro chemical cell having a high capacitance and a good lifetime characteristic through  
5 employing the above-described porous separator.

To accomplish the object, there is provided in the present invention a porous separator comprising a porous polymer layer and a polymer binder substantially uniformly dispersed on 1-80% range of a surface portion of the porous polymer layer.

10 Particularly, as the porous polymer layer which may be used in the present invention, a porous polyolefin layer, a porous polyvinylidene fluoride layer, a rayon paper, a pulp paper, a porous polytetrafluoroethylene layer, a polyester non-woven fabric, a glass fiber paper, a porous inorganic layer etc. may be mentioned. These may be used alone or in combination thereof.

15 The other object of the present invention is accomplished by a method of manufacturing a porous polymer comprising the steps of coating a solution containing a polymer binder onto a porous polymer layer and removing a solvent.

As for the coating method, a spraying method, a dipping method, a doctor blade method, a silk screen printing, an ink jet printing, etc. can be applied.

20 The further another object of the present invention is accomplished by a method of manufacturing an electro chemical cell of an energy storage system. A solution containing a polymer binder is coated onto a porous polymer layer. Then, a solvent is removed to manufacture a porous separator. Then, the porous separator is attached onto an electrode.

25 The still further another object of the present invention is accomplished by an electro chemical cell comprising a cathode, an anode positioned from the cathode with a predetermined distance and a porous separator provided between the cathode



and anode. The porous separator includes a porous polymer layer and a polymer binder substantially uniformly dispersed on a surface portion of the porous polymer layer. The electro chemical cell also includes an electrolyte which could not dissolve the polymer binder.

5        According to the present invention, the porous separator including a porous polymer layer and a polymer binder component uniformly dispersed on the surface of the porous polymer layer is used for the manufacture of an electro chemical cell. Various kinds of cells having various shapes can be advantageously manufactured and an impregnation of an electrolyte is advantageous. Further, adhering strength  
10       between an electrode and a separator is improved to heighten a capacity and improve a cyclelife characteristic of thus manufactured cell.

### **Brief Description of Drawings**

15       The above objects and advantages of the present invention will become more apparent by describing preferred embodiments in detail with reference to the attached drawings in which:

FIGS. 1A & 1B illustrate a separator on which a binder is dispersed according to the present invention, in which FIG. 1A is a schematic planar view and FIG. 1B is a schematic cross-sectional view;

20       FIGS. 2A-2D illustrate structures of electro chemical cells using a separator according to the present invention, in which FIG. 2A corresponds to a unit cell, FIG. 2B corresponds to a bi-cell, FIG. 2C corresponds to an integrated cell of unit cells and FIG. 2D corresponds to an integrated cell of bi-cells;

FIG. 3 is a graph illustrating a cycle characteristic of a battery manufactured  
25       by using an electrode according to Example 1;

FIG. 4 is a graph illustrating a cycle characteristic of a battery manufactured by using an electrode according to Example 2; and

FIG. 5 is a graph illustrating a cycle characteristic of a battery manufactured by using an electrode according to Example 3.

### **Best Mode for Carrying Out the Invention**

5           The present will be described in detail with reference to the attached drawings below.

          The separator suggested by the present invention includes a porous polymer layer and a polymer binder dispersed on the surface of the porous polymer. The porous polymer layer has a good mechanical strength as a separator used for a  
10   general energy storage system, and also has minute pores therein so as to be filled with an electrolyte to accomplish an ionic conductive characteristic. The polymer binder dispersed on the surface of the porous polymer layer is attached to an electrode and the porous polymer layer to keep a stable contact between the electrode and the porous separator. The polymer binder material adheres to the  
15   electrode at a room temperature or under a heated condition, and the adhered state is kept after an impregnation of a cell with an electrolyte. The porous separator has a mechanical strength and an electro chemical stability, and is impregnated with an electrolyte.

          FIGS. 1A & 1B illustrate a separator on which a binder is dispersed  
20   according to the present invention, in which FIG. 1A is a schematic planar view and FIG. 1B is a schematic cross-sectional view.

          According to FIGS. 1A & 1B, a polymer binder 12 is uniformly dispersed on a porous polymer layer 10 and space is formed between the polymer binders 12.

          According to the present invention, the polymer binder material is not  
25   uniformly coated onto the surface of the separator however, the polymer binder material is present on the surface of the separator through a dispersion state. Since the polymer binder material is partially dispersed on the surface of the separator, a

space is provided after adhering the electrode and the separator through the binder. Through the space formed between the electrode and the separator, an electrolyte can be impregnated into the separator and the electrode.

The porous polymer layer used in the present invention includes a generally  
5 used polymer/separator used for a battery and a capacitor. The porous polymer layer should have a good mechanical strength to prevent an electric short due to an electric contact between a cathode and an anode and an electro chemical and thermal stability. Also, an electrolyte should be advantageously impregnated into the porous polymer layer. As for the polymer layer used for the present invention includes all of  
10 the separators generally used for a battery and a capacitor. More preferably, a porous polyolefin layer, a porous polyvinylidene fluoride layer, a rayon paper, a pulp paper, a porous polytetrafluoroethylene layer, a polyester non-woven fabric, a glass fiber paper and a porous inorganic layer can be used.

As for the polymer binder material, a material which could not be dissolved  
15 into an electrolyte and has a good adhering strength with the porous polymer layer and the electrode and an electro chemical and thermal stability, may be used. The polymer binder material includes all of the binders used for an electrode for a general battery and capacitor (condenser). In addition, polymer material used for a polymer electrolyte also can be used as for the polymer binder material.

20 For example, a butadiene-based rubber of polymer material including a polyacrylonitrile-butadiene rubber (NBR), a polystyrene-butadiene rubber (SBR), a poly (styrene-butadiene-styrene) rubber (SBS), an acrylonitrile-butadiene-styrene rubber (ABS) and polybutadien;

a synthetic or natural rubber including a polydimethyl siloxane, polyisoprene,  
25 polychloroprene, polyisobutylene and ethylene-propylene rubber;

an acryl-based resin including poly (alkyl acrylate), poly (alkyl methacrylate), poly (alkyl ethacrylate), a copolymer thereof and a mixture thereof;

a polyester-based polymer including polyethylene oxide, polyoxymethylene, polypropylene oxide, a copolymer thereof, a blend thereof;

a polyvinylether-based polymer including polyvinyl methyl ether, polyvinyl ethyl ether, polyvinyl n-propyl ether, polyvinyl n-butyl ether, a copolymer thereof  
5 and a mixture thereof;

a fluoride-based polymer including polyvinylidene fluoride, polyvinylidene fluoride-hexafluoropropane, polychloro trifluoroethylene and a copolymer with ethylene, polytetrafluoro ethylene, polyvinyl fluoride and a copolymer thereof;

a chloride-based polymer including poly (vinyl chloride) and poly  
10 (vinylidene chloride);

a benzene group-containing polymer including polystyrene and a phenol resin;

an OH group-containing polymer including polyvinyl alcohol, polyhydroxy ethyl methacrylate and ethylene-vinyl alcohol copolymer;

15 an acid group-containing polymer including polyacric acid, polystyrene sulfonic acid and polyamic acid;

a photo-synthesizable polymer including polyvinyl cinnamate;

a nitrile group-containing polymer including polyacrylonitrile, polymethacrylonitrile, a copolymer thereof and a mixture thereof;

20 a polyolefin polymer including polyethylene and polypropylene;

polyvinyl acetal, polyvinyl ketal, polyvinyl butyral, polyvinyl formal; polyester, polycarbonate, polyurethane, polyamide, polyimide and the like can be used.

In addition to the above-described material, a copolymer thereof and a  
25 mixture thereof also can be used. More preferably, the rubber-based polymer, acryl-based resin, fluoride-based polymer and chloride-based polymer can be used.

As for the polymer binder solution, a solution in which the polymer is

completely dissolved in a solvent or a dispersion in which the polymer is minutely dispersed in the solution can be used. In the solution, the polymer chain is mixed in a molecular scale with the solvent according to the solubility of the polymer component with respect to the solvent. In the dispersion, concentrated and minute  
5 particles of the polymer component are present in the solution. The size of the particles does not exceed  $100\mu\text{m}$ .

When the polymer is completely dissolved into the solution to prepare the polymer binder solution, the polymer component should have a high solubility with respect to the solvent. In addition, it is preferable that the coated solvent is easily  
10 removed by vacuum or heat. When the polymer component is dispersed into a solution, the solution is required to have a good dispersion degree with respect to the polymer component, even though the solution could not completely dissolve the polymer component. When a selection of the solution having the required property is difficult, a surfactant could be added to assist the dispersion of the polymer into  
15 the solution.

Generally, the dispersion of the polymer is possible when a polarity difference between the polymer and a solvent is not small. Solvents having both non-polar and polar parts such as ethanol, isopropyl alcohol, etc. are appropriately used because these solvents can disperse both non-polar and polar polymers. As for  
20 the surfactants, almost all the surfactants including anionic surfactant, cationic surfactant, neutral surfactant and zwitter-ionic surfactant can be used. According to the kind and amount added of the surfactant, the size of the polymer particles is determined. When the amount added of the surfactant exceeds a critical micell concentration (CMC), a dispersion phase of the polymer is formed. An appropriate  
25 amount of the surfactant is dependent on the kind of the surfactant and solvent, however, the preferred amount is in the range of about 0.01-5% by weight based on the total amount of the solution. Particularly, when water is used as the solvent and

sodium dodecyl benzene sulfonate is used as the surfactant, a rubber-based binder dispersion can be obtained by adding 0.01-2% by weight of sodium dodecyl benzene sulfonate. If the surfactant is not added, the rubber-based binder is not dispersed into water but is precipitated.

5        Adhering temperature of the porous separator on which the binder is dispersed with an electrode is determined by the glass transition temperature, melting point and cross-linking temperature of the polymer binder material. For example, since the glass transition temperature of the rubber-based binder is lower than room temperature, compression with pressure at a room temperature enables  
10 the attachment of the porous separator with the electrode. When one of the amorphous polymer including the fluoride-based polymer, chloride-based polymer and polyacrylate-based polymer is used as for the polymer binder, compression with pressure at a temperature above the room temperature enables the attachment of the porous separator with the electrode. When polystyrene is used as for the polymer  
15 binder, compression with pressure at a temperature above the glass transition temperature of the polystyrene (106°C) enables the attachment of the porous separator with the electrode.

Meantime, when the crystalline polymer binder is used, compression with pressure at a temperature above the melting point of the polymer enables an  
20 effective attachment of the porous separator with the electrode.

Preferably, the polymer binder material is not dissolved into an electrolyte and more preferably is swelled by the electrolyte to keep a gel phase. When the polymer binder is swelled by the electrolyte, a surface resistance is lowered because the binder phase does not block an ion transmission. However, when the polymer is  
25 swelled excessively, the adherence between the electrode and the separator is reduced and the surface adherence might be weakened. Accordingly, the polymer material is preferably swelled by the electrolyte to about 0-5 times of the weight of

the polymer material. When the swelling of the polymer exceeds 5 times of the weight thereof, the adherence of the electrode with the separator becomes weak. More preferably, the polymer binder is swelled by the electrolyte to about 0.2-3 times of the weight of the polymer.

5        When the adherence of the polymer binder to the electrode is obtained through heating and the porous separator is made from the crystalline polymer, the adhering temperature should not exceed the melting point of the porous separator. When the porous separator is made from the amorphous polymer, it is preferable that the adhering temperature does not exceed the glass transition temperature of the  
10    separator.

      The dispersing process of the polymer binder component onto the porous polymer layer will be described in detail, below. First, a polymer solution is prepared by dispersing or dissolving the polymer binder material into a solvent. Thus prepared dispersion or solution is dispersed on the polymer layer according to  
15    one of the following methods.

      1) Thus prepared polymer solution is sprayed on the porous polymer layer by means of a spray gun. At this time, the boiling point of the solvent should exceed 30°C. When the boiling point of the solvent is lower than 30°C, the solvent volatilizes rapidly during spraying and the spraying is disturbed or the sprayed  
20    polymer material is completely dried during spraying and could not attach to the separator. After that, the separator is passed through a drying furnace to evaporate remaining solvent. The boiling point of the solvent is lower than 200°C, and preferably is lower than 100°C. From the binder solution coated on the porous separator, the solvent is removed during passing the drying furnace, while remaining  
25    only the polymer component. At this time, if the boiling point of the solvent is low, the removal of the solvent is advantageous and so the processing time is shortened. When considering this point, acetone, methanol, ethanol, isopropyl alcohol,

tetrahydrofurane, acetonitrile, and the like can be used preferably.

Since thus obtained separator does not contain an electrolyte, the spraying process needs not be implemented under de-humidified atmosphere. However, when the polymer binder material has a humidity-absorbing property, the spraying is preferably implemented under the de-humidified atmosphere.

2) As a second method, the dispersion of the polymer binder material is coated on the porous polymer layer by using a doctor blade method. After volatilizing the solvent, the binder material is dispersed on the surface of the polymer layer.

3) As a third method, the polymer layer is dipped into a dispersion of the binder to implement a dip coating. Then, the solvent is volatilized to obtain a polymer layer on which the binder material is dispersed. Similar solvents used for the implementation of the spraying method can be used for implementing the dipping method. However, different from the spraying method, a solvent of which boiling point is lower than 30°C can be used. However, the upper limit of the boiling point of the solvent is 200°C or lower.

4) For applying a screen printing or an ink jet printing, solvents such as ethanol, water, isopropyl alcohol, tapineol, N-methyl pyrrolidone, and the like can be appropriately used. These solvents have an appropriate viscosity for the application of the screen printing and ink jet printing.

The polymer binder is coated on the porous polymer layer so that 1-80% of the surface of the porous polymer layer is covered. If less than one percent of the surface of the porous polymer layer is covered, a uniform attachment of the electrode with the separator is not accomplished. When more than 80% of the surface of the porous polymer layer is covered, an impregnation of an electrolyte into the electrode and the separator is difficult. More preferably, the polymer binder is coated so that 3-20% of the surface of the porous polymer layer is covered.



Now, an electro chemical cell is manufactured by using the porous separator on which the polymer binder is dispersed.

FIGS. 2A-2D illustrate structures of electrochemical cells using a separator according to the present invention, in which FIG. 2A corresponds to a unit cell, FIG. 2B corresponds to a bi-cell, FIG. 2C corresponds to an integrated cell of unit cells and FIG. 2D corresponds to an integrated cell of bi-cells.

A porous separator 10 is positioned between a cathode 16 and an anode 14 to obtain a unit cell (FIG. 2A) and an integrated cell (FIG. 2C) or a winding-type cell is obtained by repeatedly integrating the unit cells. Unexplained reference numerals 18 and 20, respectively, designate a current collector of anode and a current collector of cathode. When two separators are attached on both sides of the anode and then, two cathode are attached on both sides of the separators to obtain a bi-cell (FIG. 2B) and an integrated cell of the bi-cells (FIG. 2D) can be obtained by integrating the bi-cells. The integration or winding of the electrode with the separator is preferably implemented under a de-humidified atmosphere, however, could be implemented under a normal atmosphere from which humidity is not removed.

After completing assembly of the cell, an electrolyte is injected into the cell to fill the electrode and separator with the electrolyte. Through the portion where the polymer binder component is not present, the electrolyte is rapidly impregnated into the electrode and separator and is used to swell the polymer binder. After that, the cell is put into a can or a pack and a sealing is implemented to complete the manufacture of the cell.

The porous separator of the present invention can be diversely applied for the manufacture of a primary battery, a secondary battery, a capacitor, etc. More preferably, the porous separator can be used for the manufacture of a cell for a lithium secondary battery which employs a cathode made by using  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , etc. Further, the porous separator also can be used for the manufacture of

a cell employing a cathode containing sulfur or an organic sulfide compound.

The preferred example of the present invention will be described in more detail, below. However, it should be understood that the present invention is not limited to the following examples.

5       <Example 1>

Polybutadiene-styrene rubber was dispersed into water into which a surfactant had been added. The concentration of the polymer component was 8% by weight. The rubber solution was sprayed on a porous polypropylene separator (celgard 3501; trade name manufactured by Hoechst) by using a spray gun. The  
10 rubber deposited separator passed through a drying furnace to evaporate water and then was dried in a vacuum oven of 60°C for one day to remove residual solvent. Thus manufactured separator had a characteristic of adhering to cathode and anode at the room temperature.  $\text{LiCoO}_2$  active material was used as for the cathode and MCMB active material was used as for the anode.

15       Cathode/separator/anode was subsequently integrated by using the adhering characteristic of the separator to form a cell. Then, 1M of  $\text{LiPF}_6$  in EC/PC/DMC = 2/1/2 solution was added into the cell and thus obtained cell was put into an aluminum laminated plastic pack. Then, a sealing process was implemented.

FIG. 3 is a graph illustrating a cycle characteristic of a battery manufactured  
20 by using an electrode according to Example 1. Both of charging rate and discharging rate were 1.0C when measured at the room temperature.

<Example 2>

Polybutylmethacrylate was dissolved into acetone so that the concentration of  
25 thus prepared solution was 10% by weight. Polybutylmethacrylate solution was sprayed on a porous polypropylene separator (celgard 3501; trade name manufactured by Hoechst) by using a spray gun. Thus obtained

polybutylmethacrylate deposited separator passed through a drying furnace to remove acetone. On thus obtained separator, polybutylmethacrylate was uniformly dispersed. The polybutylmethacrylate binder material did not exhibit an adhering property at a room temperature, however, exhibited that at a temperature of 60°C or  
5 over. An integrated cell was obtained by compressing the separator, a cathode and an anode with pressure at 80°C. LiCoO<sub>2</sub> active material was used for the manufacture of the cathode and MCMB active material was used for the manufacture of the cathode.

Then, 1M of LiPF<sub>6</sub> in EC/PC/DMC = 2/1/2 solution was added into the cell  
10 and thus obtained cell was put into an aluminum laminated plastic pack. Then, a sealing process was implemented. FIG. 4 is a graph illustrating a cycle characteristic of a battery manufactured by using an electrode according to Example 2. Both of the charging rate and discharging rate were 1.0C when measured at the room temperature.

15 <Example 3>

The polymer binder solution described in Example 1 was sprayed on one surface of a separator and the polymer binder solution described in Example 2 was sprayed on the other surface of the separator. A cathode was attached on one side where polybutadiene-styrene rubber had been dispersed and an anode was attached  
20 on the other side where polybutylmethacrylate had been dispersed to obtain an integrated-type cell. When integrating the cell, the anode and the separator were compressed with heat at 80°C and the cathode and the separator were compressed with pressure at a room temperature. LiCoO<sub>2</sub> active material was used for the manufacture of the cathode and MCMB active material was used for the  
25 manufacture of the anode.

Then, 1M of LiPF<sub>6</sub> in EC/PC/DMC = 2/1/2 solution was added into the cell and thus obtained cell was put into an aluminum laminated plastic pack. Then, a

sealing process was implemented. FIG. 5 is a graph illustrating a cycle characteristic of a battery manufactured by using an electrode according to Example 3. Both charging rate and discharging rate were 1.0C when measured at room temperature.

5 The reason why different binders were used at both sides of the polymer layer as in Example 3 is that the adhering strength to the cathode and anode is different according to the polymer. In addition, the electro chemical stability range at the cathode and that at the anode are different. Accordingly, even though the polymer component has a good electro chemical stability and a good adhering strength to the cathode, the same polymer component might have a weak electro chemical stability  
10 and a weak adherence to the anode. At this time, a polymer material having a good electro chemical stability and a good adhering strength to anode is dispersed on the surface of the separator to obtain a good performance.

As described above, a polymer binder material imparts an adherence between an electrode and a separator according to the present invention. However, different  
15 from the conventional method, the polymer binder material is coated by various methods such as a spraying method on a separator and then the solvent is completely evaporated before attaching with an electrode. That is, a separator on which a binder component is uniformly dispersed is manufactured and then, thus obtained separator is attached to an electrode. Therefore, there's no problem that the structure of the  
20 binder layer is changed after forming the separator. In addition, a resin solution is coated on the polymer layer and the solvent contained therein is evaporated and then the binder layer is attached to the electrode according to the present invention. Therefore, no deviation on an internal structure of a cell according to the difference of the evaporation rate of the solvent occurs during the attachment of the binder and  
25 electrode.

The separator described in the present invention does not contain an electrolyte but is composed on a porous polymer layer and a polymer binder

component. Therefore, the physical property of the separator due to the evaporation of the electrolyte does not change. In addition, the manufacture of the separator or the assembling of the cell needs not to be implemented under a dried room and so the productivity is good.

5           Meantime, the polymer material is mixed with a solvent and then is coated on the porous separator according to the present invention. Therefore, the binder material is not present at the inner portion of the separator but is present at the surface portion of the separator. In addition, not the whole surface of the separator is coated with the binder material but the binder material is dispersed on a partial  
10   portion of the surface. Accordingly, the impregnation of the electrolyte is advantageous.

          In addition, the rubber or binder component is not coated on the whole surface of the separator but is uniformly dispersed according to the present invention. Therefore, the electrolyte is easily impregnated into the inner portion of the  
15   separator and the electrode through the portion where the binder component is not present by means of a capillary phenomenon. Further, when the binder component is dispersed on the separator as described in the present invention, the binder component is positioned on uniform surface of the separator and so, almost all amount of the binder component is present above the contacting surface with an  
20   electrode to exhibit a good adhering strength.

          While the present invention is described in detail referring to the attached embodiments, various modifications, alternate constructions and equivalents may be employed without departing from the true spirit and scope of the present invention.

## CLAIMS

1. A porous separator comprising a porous polymer layer and a polymer binder substantially uniformly dispersed on 1-80% range of a surface portion of said porous polymer layer.  
5

2. A porous separator as claimed in claim 1, wherein said porous polymer layer is at least one selected from the group consisting of a porous polyolefin layer, a porous polyvinylidene fluoride layer, a rayon paper, a pulp paper, a porous polytetrafluoroethylene layer, a polyester non-woven fabric, a glass fiber paper and a porous inorganic layer.  
10

3. A porous separator as claimed in claim 1, wherein said polymer binder is one compound selected from the group consisting of:

15 a butadiene-based rubber material including a polyacrylonitrile-butadiene rubber (NBR), a polystyrene-butadiene rubber (SBR), a poly(styrene-butadiene-styrene) rubber (SBS), an acrylonitrile-butadiene-styrene rubber (ABS) and polybutadien;

a synthetic or natural rubber including a polydimethyl siloxane, polyisoprene, polychloroprene, polyisobutylene and ethylene-propylene rubber;  
20

an acryl-based resin including poly (alkyl acrylate), poly (alkyl methacrylate), poly (alkyl ethacrylate), a copolymer thereof and a mixture thereof;

a polyester-based polymer including polyethylene oxide, polyoxymethylene, polypropylene oxide, a copolymer thereof, a blend thereof;

25 a polyvinylether-based polymer including polyvinyl methyl ether, polyvinyl ethyl ether, polyvinyl n-propyl ether, polyvinyl n-butyl ether, a copolymer thereof and a mixture thereof;

a fluoride-based polymer including polyvinylidene fluoride, polyvinylidene fluoride-hexafluoropropane, polychloro trifluoroethylene and a copolymer with ethylene, polytetrafluoro ethylene, polyvinyl fluoride and a copolymer thereof;

a chloride-based polymer including poly (vinyl chloride) and poly(vinylidene chloride);

a benzene group -containing polymer including polystyrene and a phenol resin;

an OH group-containing polymer including polyvinyl alcohol, polyhydroxy ethyl methacrylate and ethylene-vinyl alcohol copolymer;

an acid group-containing polymer including polyacrylic acid, polystyrene sulfonic acid and polyamic acid;

a photo-synthesizable polymer including polyvinyl cinnamate;

a nitrile group-containing polymer including polyacrylonitrile, polymethacrylonitrile, a copolymer thereof and a mixture thereof;

a polyolefin polymer including polyethylene and polypropylene;

polyvinyl acetal, polyvinyl ketal, polyvinyl butyral, polyvinyl formal, polyester, polycarbonate, polyurethane, polyamide and polyimide.

4. A method of manufacturing a porous separator comprising the steps of:

coating a solution containing a polymer binder onto a porous polymer layer; and  
removing a solvent.

5. A method as claimed in claim 4, wherein said coating is implemented by a spraying method, a dipping method, a doctor blade method, a silk screen printing or an ink jet printing.

6. A method as claimed in claim 4, wherein said solution containing said polymer binder further comprises 0.01-5% by weight of a surfactant based on the total amount of said solution.

5

7. A method of manufacturing an electro chemical cell comprising the steps of:

coating a solution containing a polymer binder onto a porous polymer layer;

removing a solvent to manufacture a porous separator; and

10

attaching said porous separator onto an electrode.

8. A method of manufacturing a cell as claimed in claim 7, wherein said polymer binder is a rubber binder and said attaching of said porous separator onto said electrode is implemented by pressurizing at a room temperature.

15

9. A method of manufacturing a cell as claimed in claim 7, wherein said polymer binder is an amorphous polymer including a fluoride-based polymer, a chloride-based polymer and a polyacrylate-based polymer, and said attaching of said porous separator onto said electrode is implemented by pressurizing at a temperature above a glass transition temperature of said polymer binder.

20

10. A method of manufacturing a cell as claimed in claim 7, wherein said polymer binder is a crystalline polymer, and said attaching of said porous separator onto said electrode is implemented by pressurizing at a temperature range of from a melting point of said crystalline polymer to a melting point of said porous polymer layer.

25



11. An electro chemical cell comprising:  
a cathode;  
an anode positioned from said cathode with a predetermined distance;  
a porous separator provided between said cathode and anode, said porous  
5 separator including a porous polymer layer and a polymer binder substantially  
uniformly dispersed on a surface portion of said porous polymer layer; and  
an electrolyte which does not dissolve said polymer binder.

12. An electro chemical cell as claimed in claim 11, wherein a swelling  
10 degree of said polymer binder by said electrolyte is 0-5 times of a weight of said  
polymer binder.

13. An electro chemical cell as claimed in claim 11, wherein said polymer  
binder is swelled by said electrolyte to keep a gel state.

15

14. An electro chemical cell as claimed in claim 11, wherein said electro  
chemical cell is a primary battery, a secondary battery or a capacitor.

FIG. 1A

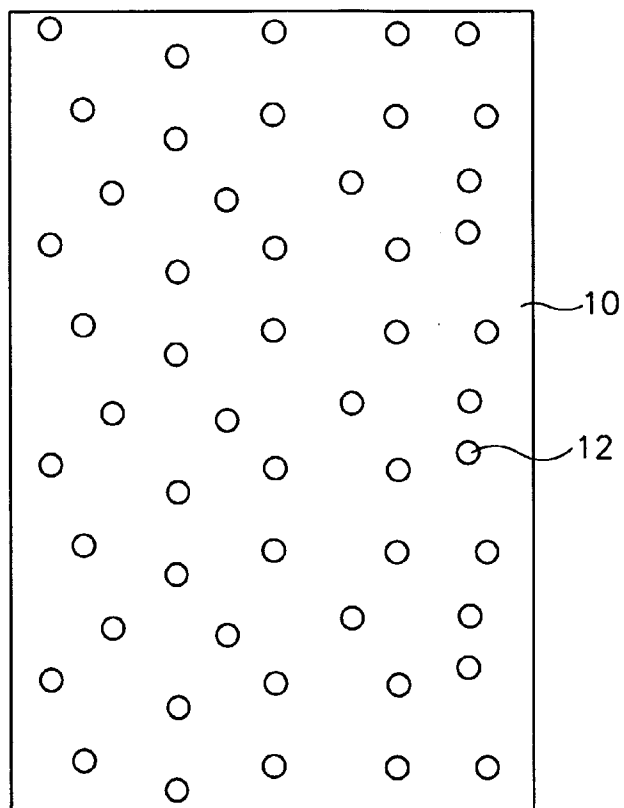


FIG. 1B

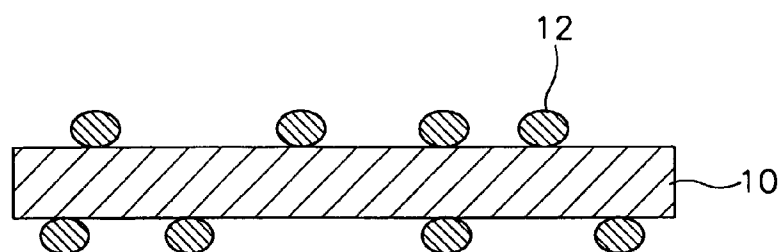


FIG. 2A

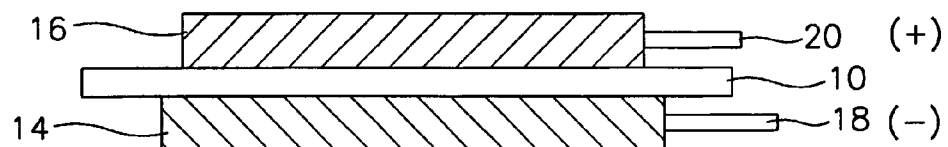


FIG. 2B

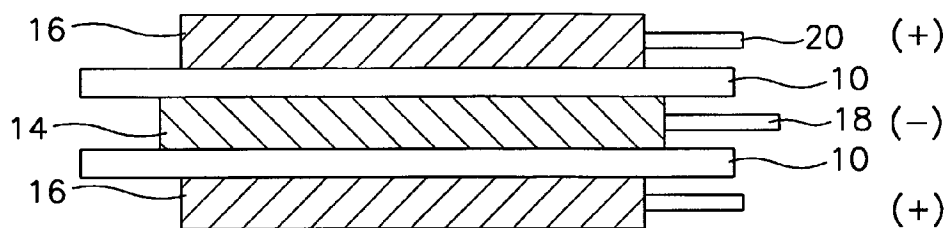


FIG. 2C

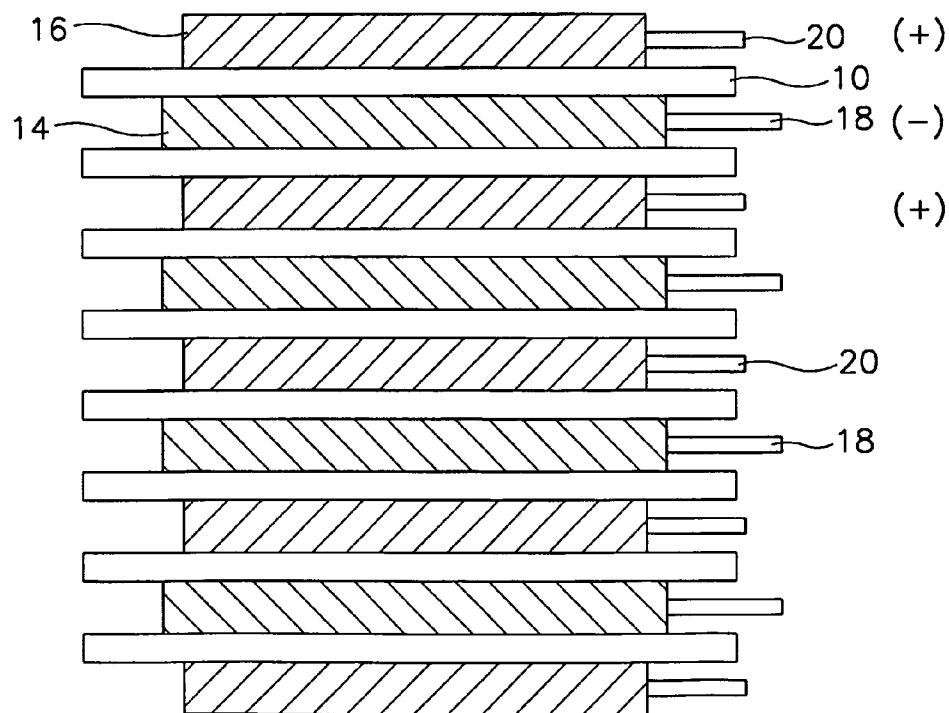


FIG. 2D

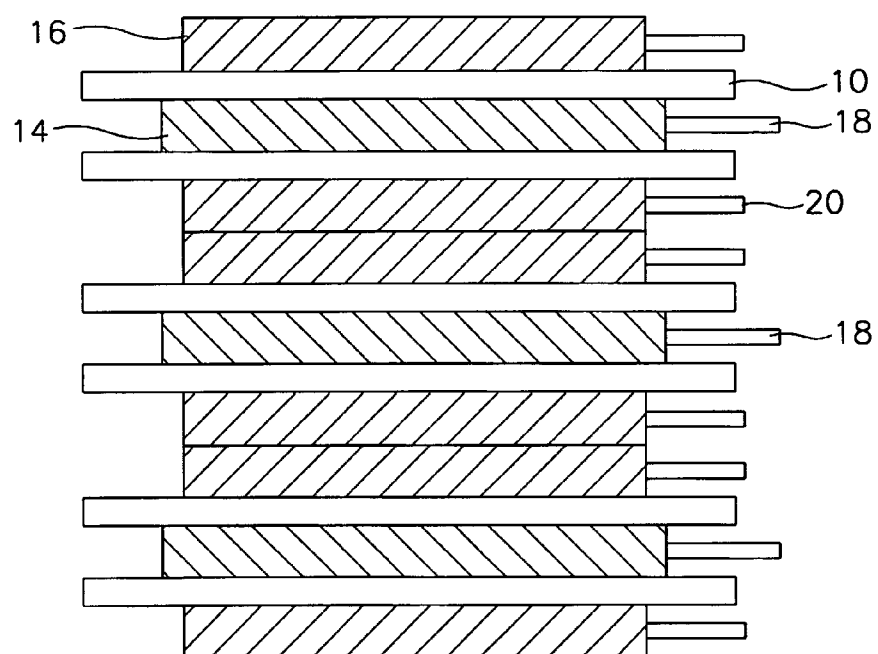


FIG. 3

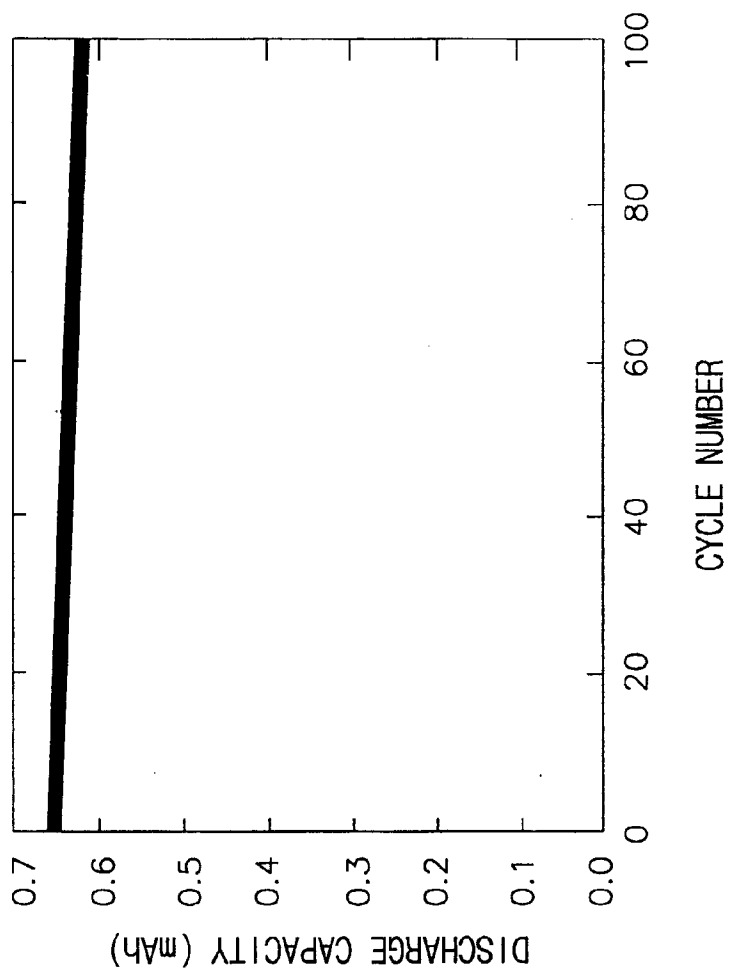


FIG. 4

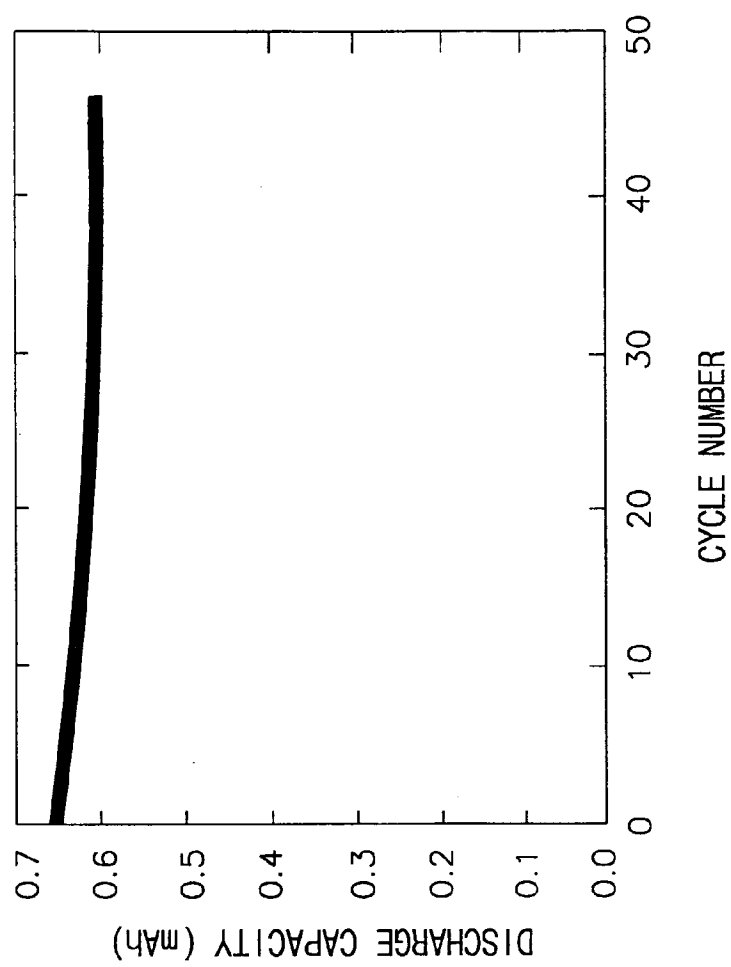
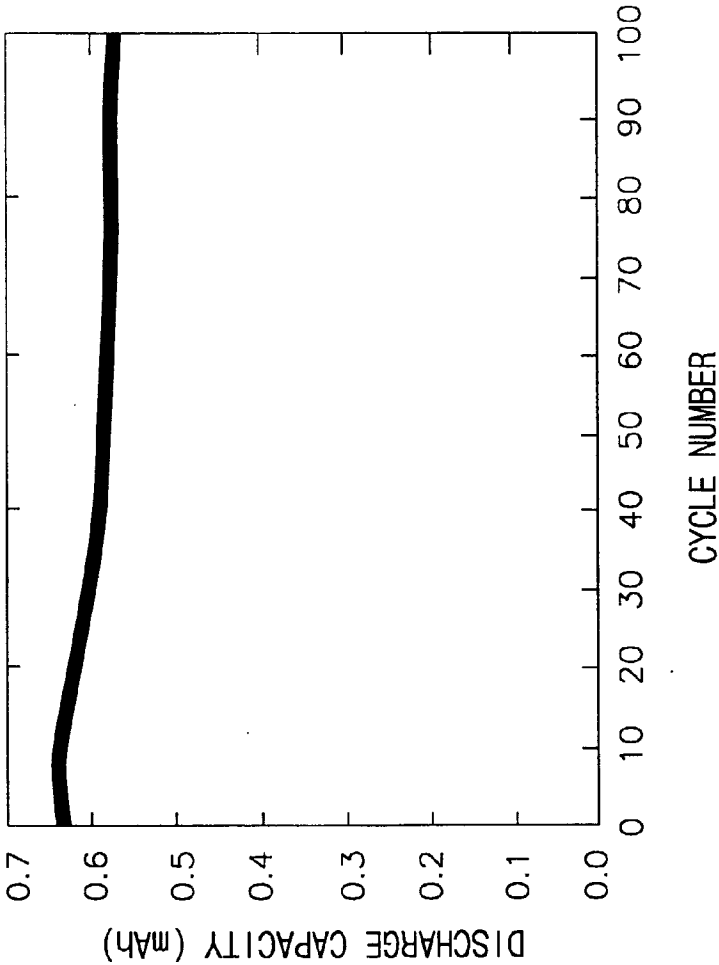


FIG. 5





## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/KR 01/01825

## CLASSIFICATION OF SUBJECT MATTER

IPC<sup>7</sup>: H01M 2/16, 2/14

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC<sup>7</sup>: H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Questel WPI and EPODOC, STN Patdpa, Depatisnet

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5478677 A (CHOI et al.) 26 December 1995 (26.12.95) <i>claims 1-8, abstract.</i>	1-9,11,14
Y	US 5368614 A (LIM, H.S.) 29 November 1994 (29.11.94) ) <i>claims 1-12, abstract.</i>	1-9,11,14
Y	US 4371596 A (SHEIBLEY, D.W.) 1 February 1983 (01.02.83) <i>claim 1 and abstract.</i>	1-9,11,14
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Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents:

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„&amp;“ document member of the same patent family

Date of the actual completion of the international search

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**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

PCT/KR 01/01825

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